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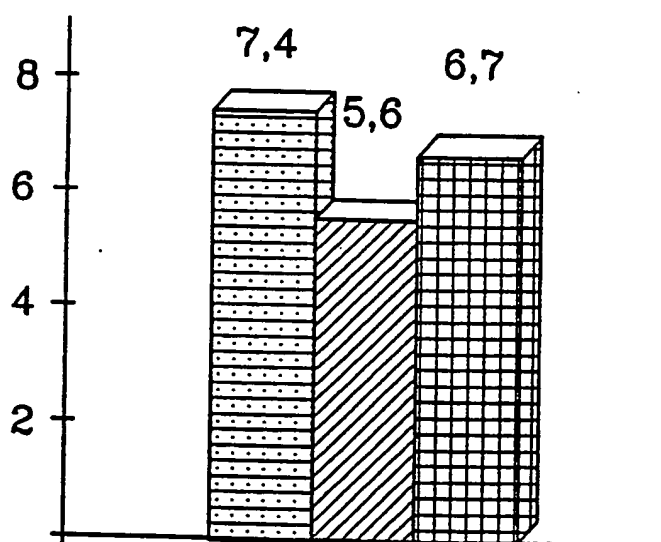
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(54) Title: COLLECTOR CHEMICAL FOR DEINKING OF WASTE PAPER



-  Collector according to the invention
-  Commercial collector
-  Soap

(57) Abstract

Collector chemical for deinking of waste paper according to the flotation process and which consists of a polyester obtained through reaction between 1) polyalkylene glycol, 2) di- and/or tricarboxylic acid and/or anhydrides thereof and 3) tall oil, said polyester having a molecular weight between 3000 - 10000.

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COLLECTOR CHEMICAL FOR DEINKING OF WASTE PAPERBackground of the invention

5

Waste paper has in later years become more and more important as raw material for paper pulp manufacture. One reason is that the supply of cellulose does not correspond to the demand of the paper industry, i.e. one compensates the shortage of pulp fibers by using waste paper. Another important reason is that the energy cost has become increasingly higher. Besides the collecting of waste paper has increased, since people are more conscious about environmental aspects today. The increased use of more complex printing ink and the increasing energy costs makes it necessary to develop more cost efficient deinking chemicals.

In order to remove printing ink from waste paper there are mainly two methods that are used, viz. the washing process and the flotation process. These two methods differ mainly in the separation of the ink.

The flotation process is most common in Europe and in South-east Asia. It gives a high yield of fibers and filler. Other advantages are environmental aspects, such as a closed water system, a low water consumption and that contaminants are obtained in concentrated form. Disadvantages with this process are the relatively high capital - and chemical costs. These costs are however compensated by the high yield, so that as a whole an economically advantageous system is achieved. The flotation process requires a careful supervision, i.e. depending on that it is sensitive to variations in the composition of the waste paper pulp. The method is mainly used when the recovered fiber mass is to be used for manufacture of newsprint paper.

The washing process is dominating in the United States and

Canada. In this process filler and fine material are also removed besides the printing ink. This is a drawback in the manufacture of newsprint paper, since the yield is bad. However it is an advantage when soft paper for sanitary purposes is to be produced. An advantage with this method is its insensitiveness for differences in the composition of the waste paper pulp. Besides the capital- and chemical costs are lower than for the flotation process.

- 10 In the washing process it is important that the printing ink is kept as dispersed and stable as possible, which is provided by high admixture of non-ionactive tensides. Washing is performed by diluting the pulp mixture to low concentrations and then watering it down to higher concentrations in
15 a water extractor, a washing filter.

The flotation process comprises several steps, the most important of which are:

1. release of ink from the fibers.
- 20 2. dispersion of the ink particles.
3. separation of ink from the fiber - ink - suspension, i.e. flotation.

In the dissolver the ink is removed from the fibers. The waste paper is here mixed with water and chemicals. The paper is disintegrated into separate fibers with adhering printing ink. The added caustic liquid gives a saponification of the surface layer of the binding agent of the printing ink, which contributes to an electrostatic repulsion between the carboxylic groups in the printing ink and on the surfaces of the fibers. This together with the softening provided by the ink components, facilitates the release of the printing ink. At the same time mechanical energy is supplied.

35

The caustic liquid also helps to disperse the ink to small ink particles, but a good wetting of the ink is also requi-

red. This is achieved by a wetting agent, which can be a non-ionic tenside, which helps the liquid to penetrate the paper. The tenside is also absorbed on the ink particles and stabilizes these so that reprecipitation is avoided. However
5 dispersion and stabilization may not occur to well, since in such case flotation can be made difficult. This is the next step in the process.

In order to enable separation of dispersed ink particles
10 their surface properties must be changed, which is made by a collector agent. The collector increases the hydrophobic character and creates an electro - chemical attraction to the air bubbles. The flotation is made in a flotation cell. Air is blown into the pulp and the ink particles then colli-
15 de with and stick to the air bubbles, which flow to the surface. A foam layer is created there, which is then separated.

The following chemicals are used in the deinking:
20

Sodium hydroxide (NaOH).

Sodium hydroxide is one of the most important deinking chemicals. In high concentration the caustic liquid contributes to break hydrogen bonds, swell the fibers and release
25 the printing ink. The NaOH saponifies the surface layer of the binding agent of the printing ink, i.e. an alkaline hydrolysis takes place. This involves electrostatic repulsion between the carboxylic groups in the printing ink and on the fiber surface. The printing ink is released and
30 dispersed. At the flotation pH is raised to 10 - 11 by adding the caustic liquid.

Hydrogen peroxide (H₂O₂)

Hydrogen peroxide is used both for bleaching the fibers and
35 for oxidizing possible organic contaminants. It has a great importance for the deinking process, since it contributes to breaking the strong bonds in the printing ink. At high

temperatures the instable hydrogen peroxide decomposes.

Water glass (Sodium silicate Na_2SiO_3)

Water glass effects the flotation process in many different
5 ways. It acts as a wetting agent, printing ink dissolver, pH
buffer, corrosion inhibitor and complex former which bonds
different metals. When adding water glass the collecting
effect of the fatty acids are considerably increased and the
reprecipitation of the printing ink on the fibers are redu-
10 ced. The instable hydrogen peroxide is stabilized by water
glass.

Surfactants

The surfactants have different functions:

- 15 * the wetting agent; reduces the surface tension
* the frothing agent; stabilized the air bubbles
* the collector; agglomerates and hydrophobizes the printing
ink.

20 Surfactants thus contribute to release the printing ink from
the fibers and then prevent that the printing ink is repre-
cipitated thereon.

The collector shall destabilize the effect of the dispersant
25 on the printing ink, before flotation of the pulp. The added
collector increases the hydrophobic character of the ink
particles and creates electro - chemical attraction to the
air bubbles. The function of the collector is thus to aggro-
merate and hydrophobize the printing ink effectively.

30

There are different types of :

- * Soap
* Synthetic collectors (advanced synthesis technique)
* Semisynthetic collectors (further refinement of fatty
35 acids).

The border - line between synthetic and semisynthetic col-

lectors is however diffuse.

When soap is used as collector there is one requirement. The fatty acids must be treated with calcium - and magnesium ions in order to function effectively. These ions can later in the process cause problem in the process. Up to now soap is the collector that has caused the best brightness, i.e. the best deinking result. Soap is relatively cheap and there are many distributors.

10

One of the disadvantages is that at least 30% of the added soap goes along with the paper, which gives poor runnability and coatings. Soap is besides difficult to handle. Use of soap causes high fiber losses, which means that the amount of raw material to the process has to be increased.

Both synthetic and semisynthetic collectors have the advantage of being independent on the water hardness, i.e. calcium ions is no requirement. Therefore a better runuability can be provided. The collector gives a lower brightness and are more expensive than soap, but they often give effective deinking at a lower dose. The msot common synthetic collectors consist of strongly hydrophobic non-ionic tensides, e.g. etoxylated fatty acids.

25

The mechanism of the collector could be explained in two ways. Synthetic collectors can function as a small wetting and in this way catch the printing ink, but there is then a risk that also fibers are catched. The collector can also due to there hydrophobic properties collect the printing ink to aggregates. The are a number of factors which influence the effect of the.

The molecular weight is an important parameter, which probably should be between 3000 - 10000. This can be controlled in e.g. a GPC (gel permeation chromatography), after finished synthesis.

35

The acid value is a measure of the number of carboxylic groups in the product (=mg potassium hydroxide per g sample). The acid value is reduced during the progress of the reaction. A low acid value indicates that most carboxylic groups have reacted which involves a hydrophobic product, which is desirable.

The hydrophobity is important for enabling the collector to selectively collect the ink particles, i.e. without bringing the fibers along. In order to regulate the hydrophobity the length of the carbon chain can be varied.

Object and most important features of the invention

The object of the present invention is to provide a collector, which fulfils the following requirements. The collector should function without admixture of calcium ions. It should not deteriorate the backwater purity with time, and thus permit recirculation of the water without deteriorating the brightness of the pulp. The collector should function selectively without negatively influencing the other chemicals. The dosing requirement must not be so exact that small variations influence the deinking process. The collector should be simple to handle and cheap to manufacture. Besides it should not give any side effects on the environment, i.e. at least partly be based on naturally occurring substances and be decomposable.

This has according to the invention been provided by a polyester produced by reaction between 1) polyalkylene glycol, 2) di - and/or tricarboxylic acid and/or anhydrides thereof and 3) tall oil, said polyester having a molecular weight between 3000-10000.

35

Description of the drawings

Figure 1 is a block diagram showing the increase of bright-

ness at flotation tests with the collector according to the invention, a commercial collector and soap.

Figure 2 shows flotation graphs for the collector according to figure 1.

- 5 Figure 3 shows flotation graphs for the collector according to the invention in different additive amounts.

Theoretical background

- 10 A polyester is an organic compound formed through reaction between alcohols and acids. The polyester is defined as a polymer with ester bond in the main chain:



or

- 15 -RCOO-RCOO-RCOO-

There are different polyesters available: linear saturated or unsaturated polyesters, branched saturated or unsaturated polyesters and saturated and unsaturated network polyesters.

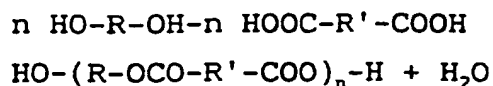
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- There are two types of polymerisation reactions, namely chain - and step polymerisation. For producing polyesters step polymerisation is used, so called condensation polymerisation. The step polymerisation is characterized by the following:

25

- * all molecules, irrespective of size, can react with each other.
- * during the whole reaction there are all molecular sizes present, i.e. there is a broad molecular weight distribution (MPD).
- * the monomers disappear early from the reaction mixture.
- * the molecular weight increases continuously during the progress of the polymerisation.
- 35 * long reaction time and high transformation are required for achieving high molecular weight and degree of polymerisation (and by that a low acid value).

In order to obtain a polymer the monomers have to be at least bifunctional, i.e. they should contain two functional groups per molecule. Direct esterification with such monomers gives:

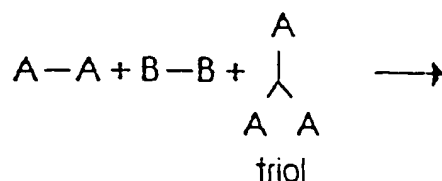


Examples of acids are maleic acid, fumaric acid and adipic acid. Common diols are ethylene glycol, propylene glycol and 1,4 - butane diol. By varying the acids and diols polyesters with different properties are obtained.

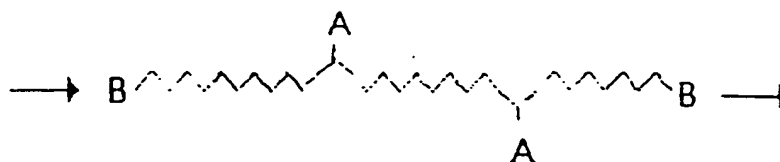
At technical production of polyesters, which often takes place at temperatures between 150°C and 200°C, one usually directly esterifies the acids with a certain excess of diol. At the same time water is removed through distillation. This is made in order to prevent a return reaction and for obtaining high polymerisation degrees. Excess of one of the monomers gives a stoichiometric unbalance, which involves a limited molecular growth, i.e. control of chain length and molecular weight is obtained. Other ways of controlling this is by means of monofunctional compounds, monovalent acid or monovalic alcohol, which stops the reaction (so called chain stopper). In all esterification reactions H_2SO_4 can be used as catalyzer.

If instead of bifunctional monomers multifunctional monomers are used, i.e. trifunctional, no linear polymers are obtained. The multifunctional monomers contain more reactive groups, and thus give branching points, which can contribute to branching and netting at the polymerisation. The final product is then a network polymer.

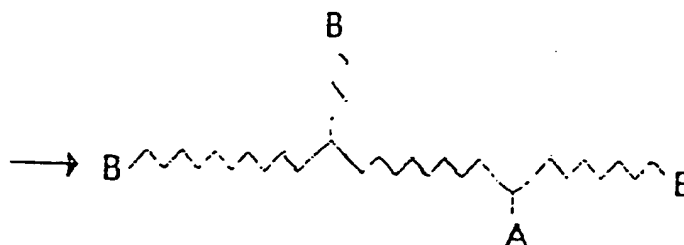
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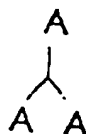
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10



15 One here speaks of a certain functionality f , e.g. $f = 3$.



20 At a certain yield (transformation) the polymer becomes sparingly soluble and forms a gel. This occurs at the so called gel point, which can be determined when the functionality is known. When 100% transformation is achieved the network consists of one single polymer molecule.

25

Under conditions that functional groups of the same kind are equally reactive and that the reactivity is independent of the molecular size, one can calculate in the same way as for bifunctional monomers. There are however exceptions, i.a. glycerol, where the secondary alcohol group is less reactive than the two primary groups.

The following chemicals have been used at the preparation of the collector according to the invention.

35 1) Polyalkylene glycol, e.g.

Polyethylene glycol PEG $HO-(CH_2-CH_2O)_n-H$

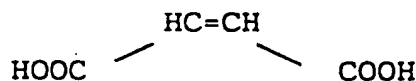
PEG occurs in many different molecular weights. We have used the mean molecular weight 300, 400 and 600, which all are liquids and PEG 1500, which is a solid compound.

5 Polypropylene glycol, PPG $\text{HO}-\text{CCH}_2-\text{CH}_2-\text{CH}_2\text{O})_n-\text{H}$.

This also occurs in different molecular weights. PPG 400, 600, 1200, 2000 and 4000 have been used. All are liquids.

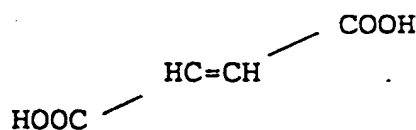
10 2) Di- and tricarboxylic acid or its anhydrides in e.g.

Maleic acid (cis-form)

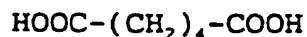


Fumaric acid (trans-form)

15

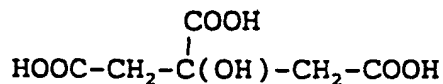


Adipic acid



20

Citric acid

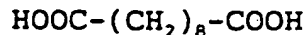


Oxalic acid



25

Sebacic acid



3) Tall oil which contains i.a. varying amounts of fatty acids and resin acids.

30

The final product is a polymer (polyester) with a mean molecular weight of 3000-10000, preferably 5000-10000.

35

By using bifunctional alcohols and acid the molar ratio should be close to 1. Tall oil is used for controlling the chain length of the final polymer.

Since we have used a simple one-stop synthesis no residual products are obtained, which should be taken care of in the manufacturing process. Only aliphatic carboxylic acids have been used, which are more easily decomposeable and less
5 toxic (cancerogenic) as compared to aromatic compounds.

Description of embodiments

A member of different collectors were prepared having the
10 following composition of raw material:

<u>Collector 1A</u>			<u>Collector 1B</u>		
	Maleic acid	102 g		Maleic acid	51 g
	PEG 400	461 g		PEG 400	230 g
5	Tall oil	35 g		Tall oil	35 g
 <u>Collector 2</u>			 <u>Collector 3</u>		
	Maleic acid	97 g		Maleic acid	70 g
	PEG 400	486 g		PEG 300	223 g
10	Tall oil	47 g		Tall oil	28 g
 <u>Collector 4</u>			 <u>Collector 5</u>		
	Maleic acid	53 g		Maleic acid	8 g
	PEG 600	365 g		PEG 1500	238 g
15	Tall oil	26 g		Tall oil	9 g
 <u>Collector 6</u>			 <u>Collector 7</u>		
	Maleic acid (90%)	46 g		Maleic acid (50%)	26 g
	Citric acid (10%)	5 g		Citric acid (50%)	42 g
20	PEG 400	231 g		PEG 400	379 g
	Tall oil	17 g		Tall oil	152 g
 <u>Collector 8</u>			 <u>Collector 9</u>		
	Citric acid	92 g		Oxalic acid	80 g
25	PEG 400	576 g		PEG 400	456 g
	Tall oil	293 g		Tall oil	66 g
 <u>Collector 10</u>			 <u>Collector 11</u>		
	Fumaric acid	102 g		Adipic acid	127 g
30	PEG 400	461 g		PEG 400	464 g
	Tall oil	35 g		Tall oil	36 g
 <u>Collector 12</u>			 <u>Collector 13</u>		
	Sebacic acid	94 g		Maleic acid	102 g
35	PEG 400	235 g		PPG 400	461 g
	Tall oil	22 g		Tall oil	35 g

5	<u>Collector 14</u>		<u>Collector 15A</u>	
	Maleic acid	53 g	Maleic acid	11 g
	PPG 600	365 g	PPG 1200	218 g
10	Tall oil	26 g	Tall oil	10 g
	<u>Collector 15B</u>		<u>Collector 16A</u>	
	Maleic acid	49 g	Maleic acid	9 g
15	PPG 1200	480 g	PPG 2000	370 g
	Tall oil	11 g	Tall oil	13 g
	<u>Collector 16B</u>		<u>Collector 17A</u>	
20	Maleic acid	28 g	Maleic acid	4 g
	PPG 2000	455 g	PPG 4000	758 g
	Tall oil	7 g	Tall oil	11 g
	<u>Collector 17B</u>		<u>Collector 18</u>	
	Maleic acid	10 g	Maleic acid	102 g
	PPG 4000	322 g	PEG 400	461 g
	Tall oil	2 g	Unitol (Tall oil)	35 g

At the manufacture of all the above collectors 1 ml sulphuric acid has been used as catalyst.

Synthesis of the collector

5

The solid and liquid initial chemicals were mixed together with the catalyst in a flange falsk. Nitrogen gas was introduced into the mixture in order to provide stirring and avoid oxidation. The vacuum suction device was then started
10 in order to reduce the pressure.

When the pressure was sufficiently reduced the flask was heated from room temperature to 150 - 200°C.

15 The synthesis was continued for about 3 hours and was controlled at regular intervals. This was made for measuring the acid value, which showed how far the reaction had proceeded. When the acid value was sufficiently low the synthesis was interrupted.

20

Another way of controlling how far the reaction has proceeded was to measure the amount of water given off, as it is a condensation reaction.

25

Flotation tests with the collector

Magazine papers and daily papers were cut in pieces of about 3,5 cm. We used the same numbers of both journal papers and daily papers in all tests.

30

Correct amounts were weighed and put in a beater together with a part of the deinking chemicals.

35

After a period of rest the paper pieces were refined to a pulp in the beater. More chemicals were mixed in and the pulp was allowed to rest for about 1 hour. The pulp was further disintegrated in another beater. The collector was

added and the slurry was brought to the cell, after which the flotation was started. Samples were taken at regular intervals from the flotation cell, said samples were later used for analysis. We controlled pH before and after the
5 flotation.

At the tests were used 100 g daily paper, 45 g magazine paper, 4 l water (40°C), 13 ml water glass, 30 ml NaOH (6,8%) and 2 ml 2% Bimex (R) (nonion tenside). The pulp was
10 allowed to rest for 10 min and was beaten in a beater for 20 min.

Then 2 ml 2% Bimex(R) and 25 ml water glass was added. The pulp was stirred and was allowed to rest 1 hour. 6 l water
15 (40°C) was added and the pulp was disintegrated during 2 minutes.

The collector (0,73 g) was added. Full dosis is 0,5% of the dry weight of paper pulp. In cases where soap was used as
20 collector 3,6 g CaCl₂ had to be added.

About 4 l water was further added when the cell is filled up.

25

Hand-sheet for optical tests

From the flotation cell was taken 500 ml mass and pH was adjusted to pH 5 with diluted sulphuric acid. The pulp is sucked off in a Büchner funnel with filter paper of 11 cm
30 diameter. Then the sheets are rolled 10 times with a stainless roller (3 clean blotting papers below and above resp.) and are allowed to dry in room temperature with a lattice weight on top. The hand sheet are made from pulp from 0, 4, 4, 8 and 16 minutes flotation time. These are used for opti-
35 cal tests.

Ink sludge

Ink sludge is collected between the times 0-4, 4-8, 8-16 minutes of flotation. The volume was measured on the respective fraction. The filter paper was dried and weighed on a balance scale. From a fraction was taken 250 ml of well mixed sludge, which was sucked off in a Büchner funnel on a filter paper that was weighed beforehand. The content in the Büchner funnel was removed and transferred to the sheet, air-dried with a lattice weight on top and weighed.

Backwater purity

Settled filtrate from the following dewaterings:

15

50 ml filtrate from 0 min. flotation (handsheet for optical tests)

50 ml filtrate from 16 min. flotation (handsheet for optical tests).

20

These were micro-filtrated (1,2 μm) with a membrane filter device (with water suction device). Optical tests were then performed on these microfilters.

25 The results of these optical tests (absolute values) are given in table 1.

Table 1

		Hand sheet for optical test				Millipore paper	
		Time (min)					
	Collector	0	4	8	16	0	16
5	00	66,2	68,3	69,2	71,2	55,2	58,6
	0 a	66,7	69,2	70,6	72,5	54,8	59,9
	0 b	66,7	69,3	70,6	72,4	56,5	59,2
	Tvål a	68,6	70,8	72,4	74,2	-	-
	Tvål b	66,9	68,7	69,6	71,7	62,1	60,6
10	Tvål c	66,5	68,3	69,7	72,1	55,9	63,8
	Tvål d	66,6	68,4	69,4	72,2	60,3	63,6
	1Aa	67,0	71,5	72,4	74,4	55,8	63,5
	1Ab	66,2	69,8	70,8	72,6	54,2	59,6
	1Ac	66,5	71,7	72,9	74,5	57,8	62,8
15	1Ad	67,1	70,1	72,1	73,5	54,4	62,5
	1Ae	67,5	70,3	71,2	73,6	54,6	62,0
	1Af	66,9	69,8	70,8	71,5	58,3	60,1
	1Ag	67,5	69,7	70,2	72,1	55,1	61,0
	1Ba	67,3	70,4	72,0	74,0	54,5	58,7
20	1Bb	67,4	70,7	71,7	73,0	54,4	62,0
	1Bc	66,7	69,6	71,2	72,7	54,4	63,0
	1Bd	66,7	68,7	72,0	72,7	57,6	65,4
	Mixed a	66,8	69,7	71,7	74,1	54,9	61,4
	Mixed b	67,1	70,5	72,2	73,6	54,1	59,7
25	2 a	66,0	67,9	68,0	69,8	56,1	60,0
	2 b	67,1	69,6	71,1	72,8	54,6	60,4
	2 c	66,6	69,8	70,7	72,8	58,3	60,6
	2 d	67,2	69,2	70,4	72,3	58,2	64,2
	3 a	67,8	70,7	72,0	73,5	54,0	59,3
30	3 b	66,0	68,8	70,5	72,1	59,6	61,8
	4 a	67,1	70,1	71,7	72,8	58,3	60,5
	4 b	67,1	70,1	72,0	73,6	56,3	62,5
	5 a	65,8	70,0	71,2	73,0	56,9	59,9
	5 b	67,8	69,9	71,2	73,7	54,6	59,8
35	6 a	67,0	70,9	72,1	73,3	54,5	65,7
	6 b	66,6	69,7	71,1	73,2	55,2	62,9
	6 c	67,7	70,5	71,1	73,0	56,9	63,5

Hand sheet for optical test

Millipore paper

		Time (min)					
Collector		0	4	8	16	0	16
	6 d	66,4	69,6	70,7	72,4	55,7	62,0
5	7 a	67,0	70,3	71,2	73,5	56,3	62,6
	7 b	67,5	71,2	72,5	74,4	54,7	60,4
	7 c	66,9	70,3	71,6	73,3	54,9	63,1
	8	68,5	72,2	73,3	74,7	55,5	59,8
	9 a	66,6	67,8	70,0	73,0	54,9	60,4
10	9 b	67,5	70,0	71,5	73,2	55,4	60,1
	10 a	67,8	70,6	72,3	73,3	57,3	60,8
	10 b	66,4	69,6	70,8	72,8	56,0	60,6
	10 b	66,4	69,6	70,8	72,8	56,0	60,0
	11 a	67,3	69,7	71,0	72,8	54,3	65,2
15	11 b	68,6	72,7	74,0	75,8	60,4	64,4
	12 a	67,1	69,4	70,3	72,0	55,9	63,4
	12 b	67,2	69,7	71,4	74,0	59,5	-
	12 c	66,7	69,8	71,2	73,2	55,9	63,0
	14	66,8	67,8	70,0	71,2	55,3	58,7
20	15B	66,9	67,8	69,0	70,8	59,8	65,7
	18 a	67,3	70,8	72,0	73,1	56,7	63,2
	18 b	67,1	69,8	71,1	72,5	56,4	61,8
	19 a	67,3	70,4	72,1	74,0	56,8	61,1
	19 b	66,8	70,7	71,4	73,7	53,8	59,1
25	19 c	67,5	71,0	72,4	73,7	57,0	60,8
	20 a	66,3	66,8	69,8	70,9	56,9	60,2
	20 b	66,3	68,1	68,2	71,0	55,0	61,4

The increase of brightness (A-brightness) for the different collectors is given in table 2.

5

Table 2

		Acid value	Δ -brightness	
Collector			Hand sheet	Backwater
	00	-	5,0	3,4
	0 a	-	5,8	5,1
10	0 b	-	5,7	2,7
	Tvål a	-	5,6	-
	Tvål b	-	5,8	-
	Tvål c	-	5,6	7,9
	Tvål d	-	5,6	3,3
15	1Aa	9	7,4	7,7
	1Ab	9	6,4	5,4
	1Ac	20	8,0	5,0
	1Ad	20	6,4	8,1
	1Ae	14	6,1	7,4
20	1Af	9	4,6	1,8
	1Ag	9	4,6	5,9
	1Ba	13	6,7	4,2
	1Bb	9	5,6	7,9
	1Bc	9	6,0	8,6
25	1Bd	9	6,0	7,8
	Mixed a	-	7,3	6,5
	Mixed b	-	6,5	5,6
	2 a	8	3,8	3,9
	2 b	8	5,7	5,8
30	2 c	11	6,2	2,3
	2 d	11	5,1	6,0
	3 a	13	5,7	5,3
	3 b	8	6,1	2,2
	4 a	10	5,7	2,2
35	4 b	10	6,5	6,2
	5 a	8	7,2	3,0
	5 b	8	5,9	5,2

				Δ -brightness	
		Collector	Acid value	Hand sheet	Backwater
5		6 a	18	6,3	11,2
		6 b	9	6,6	7,7
		6 c	9	5,3	6,6
		6 d	9	6,0	6,3
		7 a	16	6,5	6,3
10		7 b	11	6,9	5,7
		7 c	11	6,4	8,2
		8	18	6,2	4,3
		9 a	59	6,4	5,5
		9 b	59	5,7	4,7
15		10 a	7	5,5	3,5
		10 b	9	6,4	4,6
		11 a	11	5,5	10,9
		11 b	11	7,2	4,0
		12 a	9	4,9	7,5
20		12 b	9	6,8	7,5
		12 c	9	6,5	7,1
		14	10	4,4	3,4
		15B	12	3,9	5,9
		18 a	12	5,8	6,5
25		18 b	12	5,4	5,4
		19 a	-	6,7	4,3
		19 b	-	6,9	5,3
		19 c	-	6,2	3,8
		20 a	-	4,6	6,4
		20 b	-	4,7	6,4

Determination of acid value

About 2 g sample was weighed in a 300 ml E-flask. 100 ml ethanol (denaturated) was added to a E-flask and 15-20 drops of phenolphthalein solution was added. The ethanol was titrated to light rose colour change by means of 0,1 M KOH (only one or a few drops). The ethanol was added to the sample and the flask was shaken until the sample was dissolved. The sample solution was filtered to rose-red colour change with 0,1 M KOH and the amount of KOH needed for the change was determined. The titration must take place quickly, since CO₂ in the air consumes KOH. A long lasting titration gives the result of a higher acid value.

In the formula below the determined values of volume and mass are inserted:

$$\text{Acid value} = (M \cdot K \cdot \text{ml}) / m \text{ mg KOH/g solution}$$

M = molecular weight

k = concentration KOH (0,1M)

ml = ml KOH required for the titration

m = mass of sample (g)

Result

The test results prove that a collector based on maleic acid, polyethylene glycol with a mean molecular weight of 400, and tall oil gave the best deinking result. The increase of brightness after 16 min. flotation was 7,4 units (according to Hunter Lab.). Corresponding values for soap was 5,6 and for commercial collector (KAO) 6,7. The increase of brightness for the collector according to the invention was thus 10% higher for the commercial collector.

Besides the flotation was functioning better with the collector according to the invention as compared to soap and commercial collector.

In fig. 1 is shown in the form of block diagram the brightness increase after 16 minutes flotation for the collector according to the invention based on maleic acid, polyethylene glycol and tall oil and for soap and commercial collector resp.

In fig. 2 is shown flotation graphs showing the brightness as a function of time for the collector according to the invention, soap and commercial collector.

The backwater purity with the collector according to the invention was besides higher.

Tests for determining the influence of different dosing amounts on the deinking result have also been performed. To every flotation there has been used 2 kg Bimex 400/ton and varying amounts of collector 1 A according to above. The added amounts were 1, 2, 3, 4 and 5 kg collector resp./ton pulp. In fig. 3 is shown flotation graphs (brightness as a function of time) for the different admixture amounts. An admixture amount of 5 kg collector/ton pulp gave about: 5% better brightness than an admixture amount of 1 kg collector /ton pulp.

25

As a summary it can be stated that the polyester according to the invention provides a collector which is very effective and gives improved deinking results as compared to soap and commercial synthetic collectors. It is besides harmless to the environment due to its composition.

30

CLAIMS

1. Collector chemical for use in deinking of waste paper according to the flotation process,
5 c h a r a c t e r i z e d i n,
that it comprises a polyester obtained through reaction between 1) polyalkylene glycol, 2) di- and/or tricarboxylic acid and/or anhydrides thereof and 3) tall oil, said polyester having a molecular weight between 3000 - 10000.
10
2. Collector chemical according to claim 1,
c h a r a c t e r i z e d i n,
that only aliphatic alcohols and carboxylic acids are used as monomers.
15
3. Collector chemical according to claim 1,
c h a r a c t e r i z e d i n,
that the polyalkylene glycol is polyethylene glycol, polypropylene glycol or mixtures thereof.
20
4. Collector chemical according to claim 1,
c h a r a c t e r i z e d i n,
that the di- and tricarboxylic acid preferably is chosen from the group consisting of maleic acid, fumaric acid,
25 adipic acid, citric acid, oxalic acid and sebacic acid.
5. Collector chemical according to any of the preceding claims,
c h a r a c t e r i z e d i n,
30 that it has a molecular weight between between 5000 and 10000.
6. Collector chemical according to any of the preceding claims,
35 c h a r a c t e r i z e d i n,
that is produced by reaction between polyethylene glycol, maleic acid and tall oil.

FIG. 1

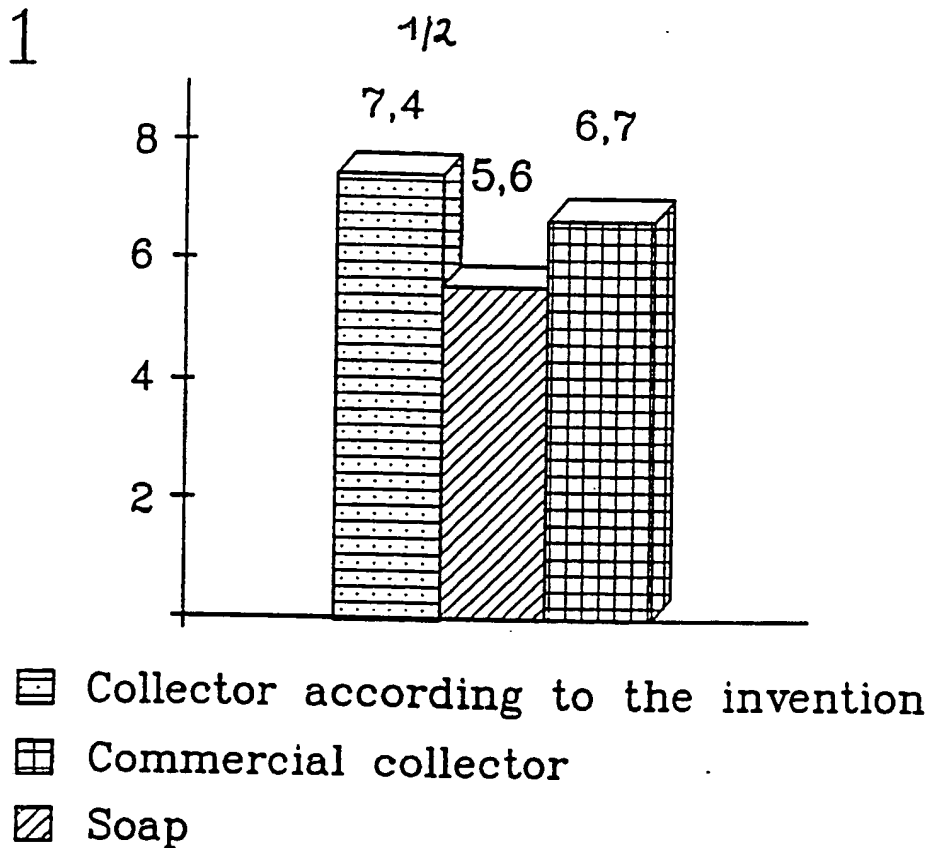
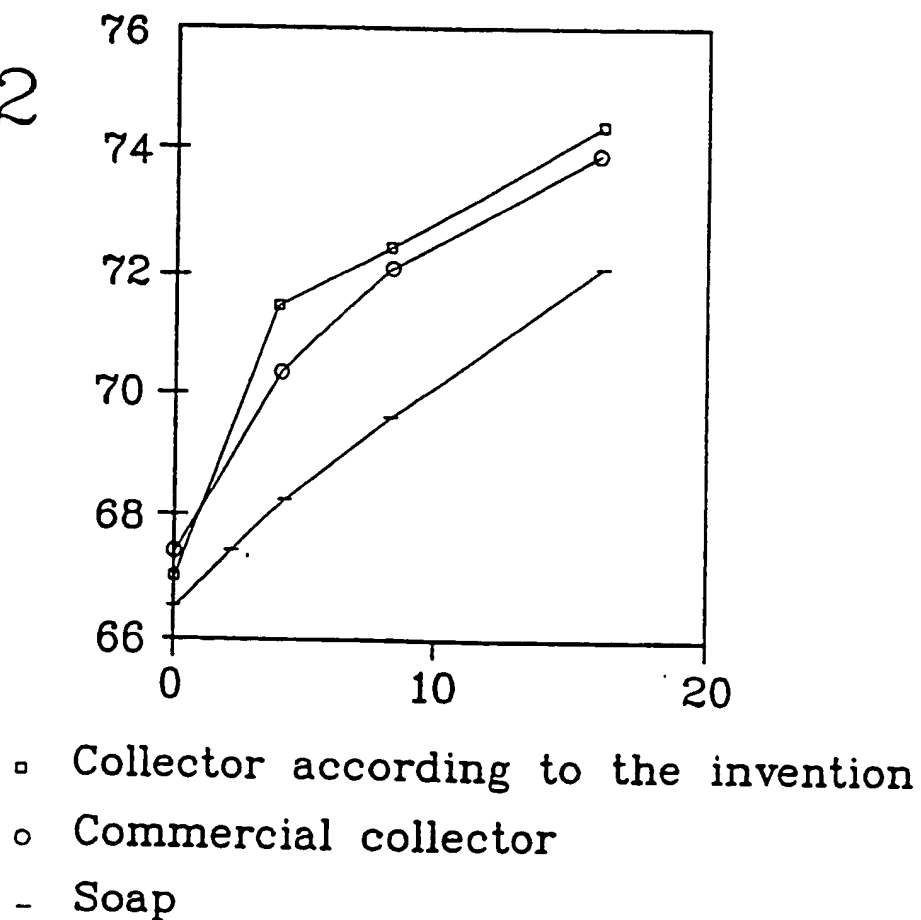
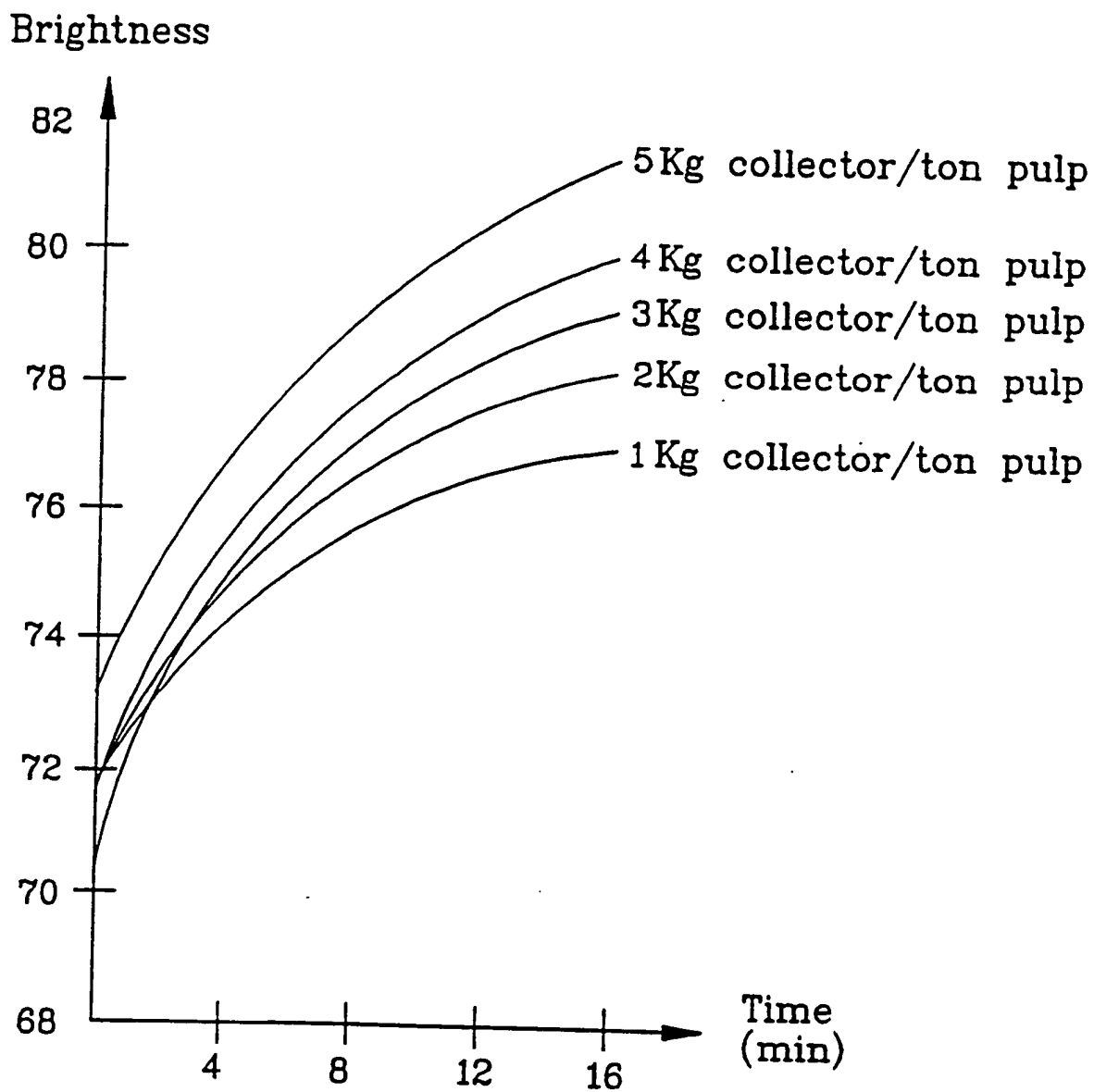


FIG. 2



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FIG. 3



INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 90/00554

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: D 21 C 5/02, C 08 G 63/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC5	C 08 G; D 21 C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched ⁸		
SE,DK,FI,NO classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	Dialog Information Services, File 351, World Patent Index 81-90, Dialog accession no. 82-73041E/35, Honshu Paper MFG KK: Toho Chem Ind Ltd: "Removing ink from waste printed paper in flotation process using cpd. obtd. by addn. polymerising alkylene oxide with mono or polyfunctional alcohol and reacting the prod. with dicarboxylic acid ", JP 57117690, A, 820722, 8235 (Basic) --	1-6
A	Dialog Information Services, File 350, World Patent Index 63-80, Dialog accession no. 78-91970A/51, Miyoshi Yushi KK: "Ink removing agent used in waste paper recycling process - is prepd. from mixed carboxylic acids and alkylene oxide deriv.", JP 53130309, A, 781114, 7851 (Basic) --	1-6
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
22nd November 1990		1990 -11- 3 0
International Searching Authority		Signature of Authorized Officer
SWEDISH PATENT OFFICE		<i>Agheta Österman Wallin</i> Agheta Österman Wallin

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	<p>Chemical Abstracts, volume 103, no. 18, 4 November 1985, (Columbus, Ohio, US), Kachan, V. et al: "Resistance of emulsion cutting fluids to microbial degradation ", see, abstract 144359s, & Khim.Tekhnol.Topl.Masel 1985, 8, 25- 8</p> <p>--</p> <p>-----</p>	1-6

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/SE 90/00554**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file on **90-11-01**
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date